PB-215 511

DETERMINATION OF FORMALDEHYDE BY THE CHROMOTROPIC ACID METHOD

Aubrey P. Altshuller, et al

Robert A. Taft Sanitary Engineering Center
Cincinnati, Ohio

1960

DISTRIBUTED BY:

NTIS

National Technical Information Service
U. S. DEPARTMENT OF COMMERCE
5285 Port Royal Road, Springfield Va. 22151

PB 215 511

DETERMINATION OF FORMALDEHYDE BY THE CHROMOTROPIC ACID METHOD

Aubrey P. Altshuller, David L. Miller and Stanley F. Sleva
Air Pollution Engineering Research
Robert A. Taft Sanitary Engineering Center
Public Health Service
U. S. Department of Health, Education and Welfare
Cincinnati 26, Ohio

Reproduced by
NATIONAL TECHNICAL
INFORMATION SERVICE
U S Department of Commerce
Springfield VA 22151

DETERMINATION OF FORMALDEHYDE BY THE CHROMOTROPIC ACID METHOD

Aubrey P. Altshuller, David A. Miller and Stanley F. Sleva
Air Pollution Engineering Research
Robert A. Taft Sanitary Engineering Center
Public Health Service
U. S. Department of Health, Education and Welfare
Cincinnati 26, Ohio

Large quantities of formaldehyde are produced both by combustion sources such as automobile exhaust [11] and by photooxidation reactions in the atmosphere.[20] Formaldehyde causes eye irritation at concentrations down to one part per million by volume.[20,23] It has been suggested that formaldehyde is likely to be one of the more important species responsible for eye irritation in Los Angeles type "smog."[20,23] Consequently, there is a continued interest in the accurate microdetermination of formaldehyde in combustion sources and in the atmosphere.

Among the various reagents proposed for the analysis of formaldehyde, chromotropic acid (1,8-dihydroxynaphthalene-3,6-disulfonic acid) has much to recommend it in terms of sensitivity and general utility. This method has been widely used for the analysis of formaldehyde itself,[7-10,13,14] methanol by oxidation to formaldehyde,[4,5,12] the methoxy group,[17] biacetyl,[22] unsaturated compounds containing double bonds in external positions by oxidation to formaldehyde, etc.,[8] both in chemical and biological systems.[6,15] A modification has been reported which results in a very stable product of high color intensity that obeys Beer's law over a wide concentration range.[24] This procedure also is both simple and rapid in its application to the analysis of formaldehyde as an atmospheric pollutant or combustion effluent.

The interference of sulfites and aldehydes, other than acrolein, has been reported to be negligible.[24] Bricker and his coworkers have investigated the interference of a number of alcohols, ketones, acids, chlorinated compounds, and a few aromatic compounds in their modifications of the chromotropic acid method.[7,9] These workers showed that most substances which may

interfere can be eliminated by adding the sample containing the formaldehyde and the possible interferences to chromotropic acid in the absence of sulfuric acid, heating to dryness to drive off the substances which might interfere, then adding the concentrated sulfuric acid and heating for 30 minutes at 100°.[9] However, this modification is considerably more complicated than the West and Sen procedure.[24] Bricker and Johnson's original method does not involve heating to dryness, but does involve the 30-minute heating. This step is not only time consuming, but also increases the interference problem owing to the long heating in an oxidizing acid. The West and Sen modification involves no heating, but instead depends on the heat of dilution at high acid concentrations to provide sufficient heat to produce stable color formation.

In the present study the previous findings[24] have been confirmed, with some minor differences in results. The study of possible interferences in this modification of the chromotropic acid method has extended to include representative members of various classes of compounds known to occur in association with formaldehyde in combustion effluents and in the atmosphere. The substances investigated as possible interferences includs a number of aldehydes and ketones, alcohols, phenols, hydrocarbons, and nitrogen dioxide.

Bricker and his coworkers were interested in determining formaldehyde in very large excess amounts of other compounds.[9] Consequently, a lack of interference at ratios of these various compounds to formaldehyde of 20,000 to 1 were of importance. However, the available analytical data on combustion sources and the atmosphere indicate that other oxygenated compounds present will exist at lower concentrations than does formaldehyde. Other gaseous substances which may possibly interfere will rarely exist at more than 1 to 10 times the formaldehyde concentration. As a result, a negligible interference at a ten-fold excess of an individual substance should be sufficient to permit a satisfactory analysis for formaldehyde.

EXPERIMENTAL DETAILS

The reagents and solutions were prepared in the manner described previously.[24] The liquid mixtures for the interference studies were prepared as follows: The liquid substances being tested were prepared in water or methanol to give a concentration 1000 times that of the formaldehyde, about 0.1 ml of this solution was added to a 10-ml volumetric flask containing 1 ml of 1% chromotropic acid reagent, 1 ml of formaldehyde solution was added, and the resulting mixture was diluted to 10 ml with concentrated sulfuric acid. The sulfuric acid concentration was maintained near 86%.

In order to make up vapor mixtures containing formaldehyde a diffusion cell with a 3.4 or 11-mm diffusion tube was partially filled with formalin solution. Air was passed through the diffusion cell at 0.5 to 1 liter/minute for 15 minutes to attain near equilibrium conditions, then the formaldehyde vapor was diverted into a collection train of impingers or bubblers.

In the portion of the work involving possible interference by olefins or nitrogen dioxide one of the olefins or nitrogen dioxide was used to fill the reservoir of an apparatus from which the gas was ejected at a known and constant rate by means of a motor driven teflon plunger. The gas passed out of the reservoir through a capillary of 0.006 inch internal diameter and about 8 inches long. This capillary, which was used to minimize diffusional flow out to the reservoir, passed through a rubber septum to a very short sidearm of a small mixing vessel. The substance being ejected was mixed with the formaldehyde vapor stream prior to the impinger or bubbler collection systems.

In later work, Mylar bags [3] were filled with formaldehyde from the diffusion cell, then the other component was vaporized into the bag by injection into an evacuated glass cylinder and flushing into the bag.

RESULTS

Stability of Formaldehyde Solutions. — A formaldehyde solution was reacted with freshly prepared chromotropic acid reagent. The absorbances of the reaction product at 580mμ when the formaldehyde solution was fresh and after the formaldehyde was 24 hours old were 2.64 and 2.61. A formaldehyde solution also was reacted with a 20-day-old chromotropic acid solution. The absorbance of the reaction product at 580 mμ, after the formaldehyde solution was two, three, and seven days old were 2.54, 2.52 and 2.28. It appears that the formaldehyde solutions are useable for one or two days after preparation but not longer.

Stability of Chromotropic Acid Solutions. — When a freshly prepared formaldehyde solution was reacted with a freshly prepared chromotropic acid reagent the absorbance as given in the previous section was 2.64. However, freshly prepared formaldehyde solution when reacted with the same chromotropic acid reagent 27 days old formed a reaction product with an absorbance of 2.54. A freshly prepared formaldehyde solution when reacted with a chromotropic acid reagent about nine months old formed a product with an absorbance of only 2.11. These results indicate that it is not advisable to use a batch of chromotropic acid solution for more than a few months. Recalibration against a standard formaldehyde solution is advisable several times during this period.

Stability of the Color of the Reaction Product. — After reaction of a 22-day-old chromotropic acid solution with a formaldehyde solution, the absorbance of the product at 580 mμ was followed for a period of eight days. The reaction times in hours and the absorbances are as follows: 2 hours, 2.53; 26 hours, 2.60; 100 hours, 2.70; 127 hours, 2.72; 148 hours, 2.73; 192 hours, 2.75.

A less complete series of measurements were made using both freshly prepared chromotropic acid and formaldehyde solutions. The reaction times

in hours and the absorbances at 580 mμ are as follows: 1 hour, 2.64; 18 hours, 2.67; 26 hours, 2.71.

It appears that a small but definite increase in absorbance occurs for a number of days. The increase amounts to less than 3% during the course of one day and less than 10% during an eight day period. These results represent a really remarkable stability for this reaction product compared to the stabilities usually observed for colorimetric products. Nevertheless, even in this instance, the calibration curves obtained on fresh solutions should not be used if the determinations must be postponed for more than 24 hours.

Reagent Concentration. — The addition of 1, 2, 3 and 4 ml of 1% chromotropic acid to 1-ml portions of an aqueous solution containing about 45% of formaldehyde and diluting with concentrated sulfuric acid resulted in absorbances at 580 mμ of 2.78, 2.79, 2.78, 2.81. These results fully confirm the previous results.[24] The reaction is insensitive to the reagent concentration for sulfuric acid concentration above 86%.

Dilution of Reaction Product. — After formation of the colored product, the solution was then diluted to various concentrations using the reagent blank. Dilution of the colored reaction product with an initial absorbance of 2.54, in the ratio of 7 to 10, 6 to 10, 5 to 10, 4 to 10, and 3 to 10 with reagent blank resulted in calculated and observed absorbances for the diluted products as follows: 1.78, 1.76; 1.52, 1.51; 1.27, 1.29; 1.015, 1.00; 0.76, 0.76. It can be seen from these results that Beer's law is followed.

Heating of Reaction Product. — Bricker and Johnson heated the reaction product for 30 minutes in their modification of the chromotropic acid method.[7] West and Sen claimed that no external heating was necessary in their procedure.[24]

In the present study heating of the reaction product for 15 and 30

minutes resulted in absorbances of 2.81 and 2.82, compared to an absorbance of 2.79 with no external heating. Consequently, heating is not necessary in the West and Sen modification, since very slight increase in absorbance will result.

Absorption Spectrum of the Reaction Product. — In addition to the absorption band at 580 mμ used for analytical purposes the reaction product forms two other bands which have absorption maxima at 480 and 370 mμ. The absorption band at 480 mμ is slightly more than half as intense as the band at 580 mμ in fresh solutions. After several days the absorption band at 480 mμ, which increases in intensity more rapidly than the band at 580 mμ, is 0.65 as intense as the band at 580 mμ. The band which appears in the ultraviolet is about as intense as the 580 mμ band.

Collection Efficiency for Formaldehyde of Various Solutions. — A series of measurements were made to determine the collection efficiency for formaldehyde of water, 1% aqueous sodium bisulfite solution and in a sulfuric acid solution of 0.1% chromotropic acid. A few measurements also were made on the collection of formaldehyde in concentrated sulfuric acid. The formaldehyde was obtained in the proper concentration range by passing air at 100 or 500 ml/minute through a diffusion cell. The gas stream was then passed through two impingers in series. The temperature of the collection solution was 25±2°. The results are given in Table I.

About 85% of the formaldehyde is collected at room temperature in the first impinger if water is used. The substantial amount of formaldehyde carried over to the second impinger indicated that a third impinger would collect additional formaldehyde but probably not more than a few per cent. The collection efficiency of the bisulfite solution is slightly superior to water alone, but a significant amount of formaldehyde still passes on to the second impinger.

The ability of 0.1% chromotropic acid in sulfuric acid to collect formaldehyde is outstanding (Table I.). Very little formaldehyde manages to pass through the first impinger. These results indicate that a single impinger will collect most of the formaldehyde in the gas stream if the chromotropic acid reagent is used. Sulfuric acid alone is almost as effective a collecting medium as the 0.1% chromotropic acid in sulfuric acid, but it has several disadvantages in the overall problems of analysis.

It has been reported previously that aqueous bisulfite solutions either at room temperatures or ice-water temperature will collect formaldehyde with very high efficiency, if an appropriate fritted glass bubbler is used. While the use of bubblers may be satisfactory with aqueous collection media, the added collection efficiency of chromotropic acid solutions for interferences can be undesirable. This problem will be discussed in detail later in this investigation.

Nitrogen Dioxide-Formaldehyde Mixtures. -- Three vapor mixtures of nitrogen dioxide and formaldehyde were prepared and the resulting formaldehyde concentration determined (Table II). Vapor mixtures containing formaldehyde alone at the same concentration in air were analyzed alternatively with the nitrogen dioxide-formaldehyde mixtures. The results indicate a slightly higher absorbance for formaldehyde in the presence of nitrogen dioxide than without it. The small difference indicates no appreciable interferences by nitrogen dioxide with the formaldehyde analysis. But, if the nitrogen dioxide is allowed contact with a phenolic type reagent such as chromotropic acid for very long periods of time, the interference of the nitrogen dioxide can become very significant.

In one additional determination, 50 µg of nitrogen dioxide was collected in 0.1% chromotropic acid-sulfuric acid medium, then 9 µg of

formaldehyde was added. This solution analyzed at 95% of the formaldehyde content found when the 9 μg of formaldehyde was added in the absence of the nitrogen dioxide.

Olefin-Formaldehyde Mixtures.-- A detailed study was made of butene-1, isobutylene, trans-2-butene and 1,3-butadiene vapor mixtures with formaldehyde in air. In addition, data were obtained on ethylene, propylene, 1-hexene and 2-methyl-1,3-butadiene vapor mixed with formaldehyde in air.

Formaldehyde would be expected to react directly with olefins via the Prins reaction in sulfuric acid medium.[2] However, the great importance of appropriate collection conditions in minimizing such interferences is clearly shown in Table III.

The previously discussed work on collection efficiency, along with the control measurements made on formaldehyde alone, all show high collection efficiencies for formaldehyde even in impingers at moderately high flow rates. A marked decrease in olefin interference is obtained by using impingers at flow rates around one liter per minute, (Table III) apparently because of reduced collection efficiency for olefins under these sampling conditions.

Ethylene and propylene at 10-to-1 excess over formaldehyde reduced the observed formaldehyde concentration by only 5 to 10%. A 15 to 20-fold excess of 2-methyl-1,3-butadiene over formaldehyde reduced the observed formaldehyde concentration by 15 or 20% when sampling into chromotropic acid solution in impingers at a moderate flow rate.

The use of water or a 1% aqueous sodium bisulfite solution as a collecting solution reduces, but does not completely eliminate the olefin interference. This is shown by the result obtained for ethylene, propylene, 2-methyl-1,3-

butadiene and 1-hexene-formaldehyde mixtures. The 10 to 20% losses of formaldehyde in sulfuric acid containing the reagent are reduced to about 5% by the use of aqueous collection solutions. Aqueous collection media have a decided disadvantage for atmospheric concentrations, since 1 ml. of aqueous solution must be diluted to 10 ml. with chromotropic acid in sulfuric acid to maintain the acidity at the proper level. Greater dilution of the sulfuric acid will reduce the overall sensitivity and reproducibility of the method. In automobile exhaust analysis, the formaldehyde concentration is high enough to permit the use of an aqueous collecting medium without difficulty.

The use of sulfuric acid alone as a collection medium is not satisfactory. Olefins and formaldehyde appear to react very appreciably in this medium. At a 10-to-1 ratio of 1-hexene to formaldehyde, only about 40% of the formaldehyde present in the vapor mixture could be detected when sulfuric acid was used for collection. At a 15 or 20-to-1 ratio of 2-methyl-1,3-butadiene to formaldehyde, less than 5% of the formaldehyde present in the vapor could be detected. Consequently, sulfuric acid not containing chromotropic acid reagent is not recommended as a collection medium.

These results show that the use of appropriate collection devices and solutions and even moderate flow rates will reduce the olefin interference with formaldehyde analysis down to quite acceptable levels. This is particularly true in automobile exhaust or atmospheric gases, in which the ratio of the more reactive olefins to the formaldehyde may be less than 6 to 1. It is even possible that the atmospheric concentration of formaldehyde will appreciably exceed the concentration of four-carbon and higher olefins.

Aldehyde or Ketone-Formaldehyde Mixtures. -- A number of aldehydes including acetaldehyde, propanal, butanal, acrolein, 2-butenal, and 2-methyl-2-butenal were reacted directly in milligram amounts with the chromotropic acid. The

saturated aldehydes and 2-methyl-2-butenal reacted to give less than one-hundredth the absorbance at 580 mμ of an equal amount of formaldehyde. 2-Butenal gives 1 or 2 percent of the response shown by an equal amount of formaldehyde. Acrolein will react with the chromotropic acid to give several percent interference with an equal amount of formaldehyde. Acrolein forms a product with a maximum in the 450 mμ range. Since formaldehyde is usually in considerable excess over any of the other individual aldehydes in combustion gases[11] and the atmosphere,[20] the interference from other aldehydes is not significant.

A number of ketones including acetone, 2-butanone, 3-pentanone, 3-methyl-2-butanone, 4-hexanone, 3-heptanone also were reacted in milligram amounts with chromotropic acid reagent. These materials reacted to give absorbance less than 0.1% that of an equal amount of formaldehyde at 580 mμ. Consequently, ketones will not interfere to any appreciable extent with the analysis of formaldehyde in combustion or atmospheric gases by the present method.

These results were confirmed by the reaction of liquid mixtures containing individual aldehydes or ketones and formaldehyde with chromotropic acid reagent. The other aldehydes or ketones were in approximately ten-fold excess over the formaldehyde. No significant change in the absorbance at 580 mμ occurred compared to the absorbance obtained by the use of an equal amount of formaldehyde alone.

Alcohol-Formaldehyde Mixtures. -- Individual alcohols in milligram amounts did not react directly with chromotropic acid reagent to give absorbances even 0.1% as high as that obtained with an equal amount of formaldehyde. Methanol [redacted]ol in ten-fold excess in mixtures with formaldehyde appear to thousand cause [redacted] no significant change in absorbance compared to pure formaldehyde.

solutions. However, higher alcohols in liquid mixtures with formaldehyde reduce the absorbance at 580 mμ appreciably.

The absorbances of mixtures of about 40 μg formaldehyde with ten-fold excesses of 2-propanol, 1-butanol, 2-methyl-2-propanol, 1-pentanol, 1-heptanol, or cyclohexanol, respectively, were as follows: 1.87, 2.15, 0.38, 2.13, 2.17, and 0.68. The formaldehyde solution alone gave an absorbance of 2.52. Consequently, all of the higher alcohols at ten fold excess reduce the apparent concentration of formaldehyde appreciably, and the branched chain alcohols are particularly reactive. These results are analogous to those obtained with the olefins, and it is reasonable to assume that both the olefins and the alcohols react with the formaldehyde by much the same mechanism.

No attempt was made to study the collection of vapor mixtures of alcohols and formaldehyde. The available data indicate that the quantities of alcohols, particularly those heavier than ethanol, in automobile exhaust or in the atmosphere must be quite small compared with the formaldehyde concentration. The total concentration of alcohols in cruise exhaust is only about one-fifth of the formaldehyde concentration.[11] Consequently the interference, even assuming efficient collection of alcohols, should not be significant.

Aromatic Hydrocarbon-Formaldehyde Mixtures. — The possible interference of aromatic hydrocarbons with the determination of formaldehyde when it is collected directly into the chromotropic acid reagent solution has been suggested previously.[19] The formaldehyde might react with the aromatic hydrocarbon in the sulfuric acid, reducing the formaldehyde available for reaction with the chromotropic acid, thus causing a reduction in apparent formaldehyde concentration.

Vapor mixtures containing formaldehyde and benzene, toluene, p-xylene, o-xylene or m-xylene were prepared. The aromatic hydrocarbon was added so as to give hydrocarbon concentrations in excess of the formaldehyde concentration

by factors ranging from about two to fourteen. The formaldehyde concentration was in the 1-5 ppm range. Several liters of each of these vapor mixtures was passed at a flow rate of one liter per minute through an impinger containing the chromotropic acid reagant.

At about 8 and 12-fold excesses of benzene, the apparent formaldehyde concentration was 80% of the actual concentration. When 8, 10 and 12-fold excesses of toluene were used, the formaldehyde concentration measured averaged about 70% of the actual value. At about a 14-fold excess of each of the xylenes, only 30 to 50% of the actual formaldehyde concentration was found. At 2 to 3-fold excesses of toluene, p-xylene, o-xylene or m-xylene, the apparent formaldehyde concentration was 80 to 90% of the actual concentration.

The present investigation proves that aromatic hydrocarbons interfere significantly when present in concentrations in excess of the formaldehyde concentration. The aromatic hydrocarbons appear to be rather efficiently retained in the chromotropic acid-sulfuric acid collection medium even at moderately high flow rates through impingers.

The interference of aromatic hydrocarbons with the analysis of formaldehyde also was investigated when water was used as the collecting medium. The flowrate used was 0.5 liters/minute. The formaldehyde concentration was in the 5 to 10 ppm by volume range. No interference occurred when a mixture containing formaldehyde and either a five or fifteen-fold excess of o-xylene or ethylbenzene was analyzed for formaldehyde. A series of vapor mixtures containing formaldehyde and a fifteen fold excess of benzene, toluene, p-xylene or m-xylene also were passed through water and analyzed for formaldehyde content. The average decrease in observed formaldehyde content was only 10%. These measurements indicate that the interference of aromatic hydrocarbons can be largely eliminated by sampling into aqueous solution and then reacting with chromotropic acid reagent.

Phenol-Formaldehyde Mixtures. — Since phenols react with formaldehyde to form polymeric products in acidic media, interference might be anticipated in the analysis of phenol-formaldehyde vapor mixtures by the chromotropic acid reagent. Owing to the solubility of phenols in water, the interference of phenols, should occur when sampling into either sulfuric acid or aqueous collecting solutions.

Vapor mixtures of formaldehyde with phenol or p-cresol were collected in chromotropic acid. The flow rates used were either 200 or 500 ml per minute. The ratio of phenolic compound to formaldehyde ranged from 8:1 to 2:1 on a weight basis in the mixtures. The formaldehyde was present in the mixtures in the 2 to 4 ppm by volume range. Even at an 8:1 ratio the observed formaldehyde concentration was only 10 to 20% less than the actual concentration. At 2:1 ratio of p-cresol to formaldehyde, no loss of formaldehyde was observed.

Vapor mixtures of formaldehyde with phenol, p-cresol, o-cresol, or m-cresol were collected at one liter per minute in water. The ratio of phenolic compound to formaldehyde was in the 3:1 to 1:1 range on a weight basis. The formaldehyde was present in these vapor mixtures in the 5 to 20 ppm by volume range. The decreases in formaldehyde concentration when compared with the actual concentration, ranged from 5 to 30% and averaged a 10% decrease.

Only a limited amount of data is available on phenols in combustion sources and the atmosphere.[21, 25] This data indicates that the total phenols actually would exist at lower concentrations than the formaldehyde in automobile exhaust [21] and incineration gases[25] and in the atmosphere.[21] Since the data obtained in the present investigation showed small losses of formaldehyde even in the presence of excess phenols, in practice the interference of phenols should be small to negligible.

Analysis for Formaldehyde in Diluted, Irradiated Automobile Exhaust. — Gas samples were passed from a dynamic irradiation chamber facility [18] through an impinger train at flow rates of one-half or one liter per minute. Each impinger contained 10 ml of the 0.1% chromotropic acid reagent in sulfuric acid. After collection, 0.5 ml of water was added to insure sufficient heating, but no appreciable change in color intensity followed. Evidently, sufficient heating occurs even when atmospheric samples at moderate relative humidities are passed through the chromotropic acid reagent.

The analyses listed in Table IV were obtained on different days, using somewhat varying engine conditions, and different irradiation periods. Consequently, they are meant primarily to illustrate the applicability of the method to samples from a synthetic atmosphere presumably equivalent to polluted atmospheres existing on the West coast of the United States. The values measured are reasonably consistent, and certainly show that appreciable concentrations of formaldehyde existed in the irradiated gases. In most localities the formaldehyde concentrations probably would be an order of magnitude lower. However, the formaldehyde concentrations in severe Los Angeles type "smogs" may well approach the formaldehyde concentrations listed in Table IV.

DISCUSSION

Sampling directly into chromotropic acid in sulfuric acid offers three major advantages. First, the sensitivity is ten times higher than if the formaldehyde is collected into aqueous solution and then diluted nine-to-one with chromotropic acid solution. Second, the procedure is extremely simple, involving only a single reagent, no dilutions or additions of other components, and no heating or prolonged reaction periods before

analysis. Third, the collection efficiency of a sulfuric acid solution of chromotropic acid is so high that only a single impinger is required.

A disadvantage of the procedure is the likelihood of interference in a sulfuric acid solvent medium. A possible second disadvantage lies in the increased care needed in handling a strong acid during the sampling period.

In sampling for formaldehyde in combustion gases a pair of impingers in series containing an aqueous collecting medium may be the sampling procedure of choice. Passing 30 liters of gas containing 0.5 ppm of formaldehyde through chromotropic acid solution results in an absorbance of approximately 1.0 (Table IV). If an absorbance of 0.2 is considered satisfactory for quantitative analysis, this intensity can be obtained by collecting the formaldehyde from 60 liters of gas containing 0.5 ppm of formaldehyde into an aqueous medium. Below the 0.5 ppm by volume level of formaldehyde it is necessary to use a very large gas volume and long sampling periods to obtain sufficient formaldehyde for analysis. Alternatively, if 3 ml of aqueous solution is added to 27 ml of chromotropic acid reagent solution, enough solution volume is available to use a spectrophotometer cell of either 5 or 10 cm optical path-length.

It is in the analysis of combustion gases for formaldehyde by direct collection into chromotropic acid that the interference problem is the most critical. This is particularly the situation in automobile exhaust. The total olefin content of automobile exhaust may exceed the formaldehyde concentration by a factor of 8 or 10. However, the results of the present investigation indicate that this olefin content need not constitute a serious interference. The aromatic hydrocarbons in automobile exhaust likewise may exceed the formaldehyde content by a factor of 5 or 10. This quantity of aromatic hydrocarbons will constitute a serious interference. Consequently, sampling into aqueous solution is the preferred procedure. Any olefin or aromatic

hydrocarbon collected in this way will still interfere when the chromotropic acid solution is added, but the collection efficiency of water for hydrocarbons is much lower than that of sulfuric acid.

Phenols and higher molecular weight alcohols if present in excess of the formaldehyde concentration will interfere somewhat in both aqueous and sulfuric acid type collecting media. However, the available data indicates that both of these classes of compounds occur in much lower concentrations than formaldehyde in most combustion sources and in the atmosphere.

It is in the atmospheric sampling situation that sampling directly into chromotropic acid is most advantageous. Formaldehyde is unlikely to exceed a few tenths of a part per million by volume in the atmosphere. In smoggy atmospheres the small interference from olefins is reduced further, since the formaldehyde present is formed in part by the consumption of olefins by photooxidation reactions.

Few data are available to estimate the ratio of aromatic hydrocarbon to formaldehyde in smoggy atmospheres. In situations similar to the irradiation conditions resulting in the formaldehyde concentrations reported in Table IV, that ratio is unlikely to exceed two to one, even without further reduction in the aromatic hydrocarbon content by photooxidation reactions. The small amount of laboratory data available indicates that xylenes may disappear by photooxidation reactions about as rapidly as olefins such as 1-butene or 1-pentene.[20]

The considerations discussed above suggest that only a small or insignificant interference by aromatic hydrocarbons and olefins will occur in the analysis for formaldehyde in smoggy atmospheres by the direct collection in chromotropic acid solution. In other gas mixtures, and particularly those with large amounts of aromatic hydrocarbons, collection into aqueous solution is advisable.

LITERATURE CITED

1. Altshuller, A.P., Cohen, I.R., Anal. Chem. 32, 802 (1960).
2. Arundale, E., Mikeska, L.A., Chem. Revs. 51, 505 (1952).
3. Baker, R.A., Doerr, R.C., Int. J. Air Poll. 2, 142 (1959).
4. Beyer, G., J. Assocn. Offic. Agr. Chemists 34, 745 (1951).
5. Boos, R.N., Anal. Chem. 20, 964 (1948).
6. Boyd. J.M., Logan, M.A., J. Biol. Chem. 146, 279 (1942).
7. Bricker, C.E., Johnson, H.R., Ind. Eng. Chem. anal. ed. 17, 400 (1945).
8. Bricker, C.E., Roberts, K.H., Anal. Chem. 21, 1331 (1949).
9. Bricker, C.E., Vail, A.H., Anal. Chem. 22, 720 (1950).
10. Eegriwe, E., Z. anal. chem. 110, 22 (1937).
11. Ellis, C., Hurn, R.W., "Oxygenated Compounds in Automobile Exhaust Gases as Shown by Chemical Analysis," to be published.
12. Fabre, R., Truhaut, R., Singerman, A., Ann. Pharm. Franc. 12, 409 (1954).
13. Kleinert, T., Srepel, E., Mikrochemic ver. Mikrochim. Acta 33, 328 (1948).
14. MacDonald, W.E., Am. Ind. Hyg. Assoc. Quart. 15, 216 (1954).
15. MacFadyen, D.A., Watkins, H.D., Anderson, P.R., J. Biol. Chem. 158, 107 (1945).
16. Mathers, A.P., J. Assoc. Offic. Agr. Chemists 38, 753 (1955).
17. Mathers, A.P., Pro, M.J., Anal. Chem. 27, 1662 (1955).
18. Rose, A.H., Brandt, C.S., J. Air Poll. Control Assoc., August, 1960.
19. Sawicki, E., Hauser, T.R., Stanley, T.W., Elbert, W., Anal. Chem., to be publ.
20. Schuck, E.A., Doyle, G.J., "Photooxidation of Hydrocarbons in Mixtures Containing Oxides of Nitrogen and Sulfur Dioxide." Report No. 29, Air Pollution Foundation, San Marino, California, October, 1959.
21. Smith, R.G., MacEwen, J.D., Barrow, R.E., Am. Ind. Hyg. Assoc. J. 20, 149 (1959)
22. Speck, J.C., Anal. Chem. 20, 647 (1948).
23. Stephens, E.R., Darley, E.F., Taylor, O.C., Scott, W.E., Int. J. Air Poll. to be published.
24. West, P.W., Sen, B., Z. anal. chem. 153, 177 (1956).
25. Yocom, J.E., Hein, G.N., Nelson, H.W., J. Air Poll. Control Assoc. 6, 84 (1956).

TABLE I. COLLECTION EFFICIENCIES OF VARIOUS SOLUTIONS FOR FORMALDEHYDE

Collecting Solution	Absorbance 1st impinger	2nd impinger	% in 1st impinger
water	0.57	0.16	78
	.75	.14	84
	.61	.13	82
	.53	.07	88
	.58	.09	86
	.53	.10	84
1% aqueous sodium	.98	.07	93
bisulfite	.93	.10	90
	1.03	.07	94
0.1% chromotropic acid	.58	.02	97
in sulfuric acid	.46	.00	100
	1.96	.01	99
	2.07	.03	99
	.88	.01	99

TABLE II. ANALYSIS OF NITROGEN-DIOXIDE FORMALDEHYDE MIXTURES

Concentration of Components, ppm			% of Calculated
Formaldehyde	Nitrogen Dioxide	Absorbance	Formaldehyde Content
4	—	0.97	
4	40	1.01	
			104
200	—	1.13[a]	
200	1000	1.21[b]	
			107
240	—	1.35[a]	
240	200	1.40[b]	
			104

[a] average of two determinations

[b] average of three determinations

TABLE III. ANALYSIS OF FORMALDEHYDE OLEFIN VAPOR MIXTURES

Olefin used	Concentration, ppm Formaldehyde	Concentration, ppm Olefin	Collection[a] Device	Flow Rate ml/minute	% of Calculated Formaldehyde Content
1-butene	10	120	bubbler	100	73[b]
	7	60	bubbler	100	83[b]
	8	60	impinger	200	90[b]
	3	24	impinger	500	92[b]
	2	12	impinger	1000	98[c]
trans-2-butene	12	120	bubbler	100	29[c]
	4	300	impinger	200	80
	.2.5	24	impinger	500	84[c]
	.2.5	120	impinger	500	54
isobutylene	15	120	bubbler	100	46[c]
	15	120	impinger	100	86[c]
	3	24	impinger	500	91[c]
	1.5	12	impinger	1000	95[c]
1,3-butadiene	15	120	impinger	100	37[d]

TABLE III cont.

Olefin used	Concentration, ppm Formaldehyde	Concentration, ppm Olefin	Collection[a] Device	Flow Rate ml/minute	% of Calculated Formaldehyde Content
	6	32	impinger	200	92[b]
	5	32	impinger	1000	99

[a] collection medium 20 ml. of 0.1% chromotropic acid in sulfuric acid

[b] average of three determinations

[c] average of two determinations

[d] average of six determinations

TABLE IV. FORMALDEHYDE ANALYSES OF DILUTED, IRRADIATED AUTOMOBILE EXHAUST

Fuel No. [a]	Flow Rate ml/minute	Total Gas Volume liters	Absorbance [b]	Total μg of Formaldehyde	Formaldehyde [c] in ppm by volume
3	500	30	0.88	17.0	0.44
3	1000	30	1.21	23.1	.63
3	1000	20	0.72	13.8	.56
5	1000	60	2.17	42.7	.58
5	1000	30	0.98	18.7	.50
5	1000	30	1.15	21.9	.59

[a] Fluorescent indicator absorption analyses in volume % of fuels.

Fuel No. 3: Saturates, 47.1; Olefins, 13.9; Aromatics, 39.0.

Fuel No. 5: Saturates, 38.8; Olefins, 22.9; Aromatics, 38.3.

[b] Measured in 1cm optical path-length cells.

[c] Assuming vapor density for monomeric formaldehyde of 1.23 g/liter at 25° and 760 mm.